THE ACID-CATALYZED DECOMPOSITION OF CITRAL

BY

MARION LUND DICKMAN

B.S., University of Illinois, 1940

M.S., University of Illinois, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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THE UNIVERSITY OF ILLINOIS, 1944

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INTRODUCTION

It has been observed that citral, the characteristic flavoring constituent of lemon oil, undergoes a relatively rapid decomposition in acidic aqueous solutions. It is the purpose of this investigation to establish the chemical nature of this degradation process and to study the kinetics of the reaction involved.

EXPERIMENTAL AND DISCUSSION

The rate of disappearance of the aldehyde group of citral was followed by using a modification of the hydroxylamine sulfate method of Schultes.[1] A dilute aqueous solution of citral was placed in a thermostat, acid was added, and 50-cc. samples were withdrawn at intervals for analysis. The acid was neutralized immediately, then excess hydroxylamine sulfate solution was added, and the sulfuric acid liberated was titrated to pH 4.25 with 0.01 N barium hydroxide solution.

$$2\ >C{=}O\ +\ (NH_2OH)_2{\cdot}H_2SO_4 \longrightarrow 2\ >C{=}NOH\ +\ H_2O\ +\ H_2SO_4$$

It was found that the disappearance of the carbonyl group of citral was first order with respect to citral concentration, and first order with respect to hydrogen ion concentration. The rate was measured at 25° and at 45°.

$$-\,d\,(\text{citral})\,/\,d\,t = k'\,(\text{citral}) = k\,(\text{citral})\,(H^+)$$

The rate of disappearance of unsaturation in citral was followed by quantitative measurement of the bromine absorbed. Excess bromine water was allowed to react with citral. Potassium iodide was then added to convert the excess bromine to iodine, and the latter was titrated with standard sodium thiosulfate.

$$Br_2 + 2\,KI \longrightarrow 2\,KBr + I_2$$

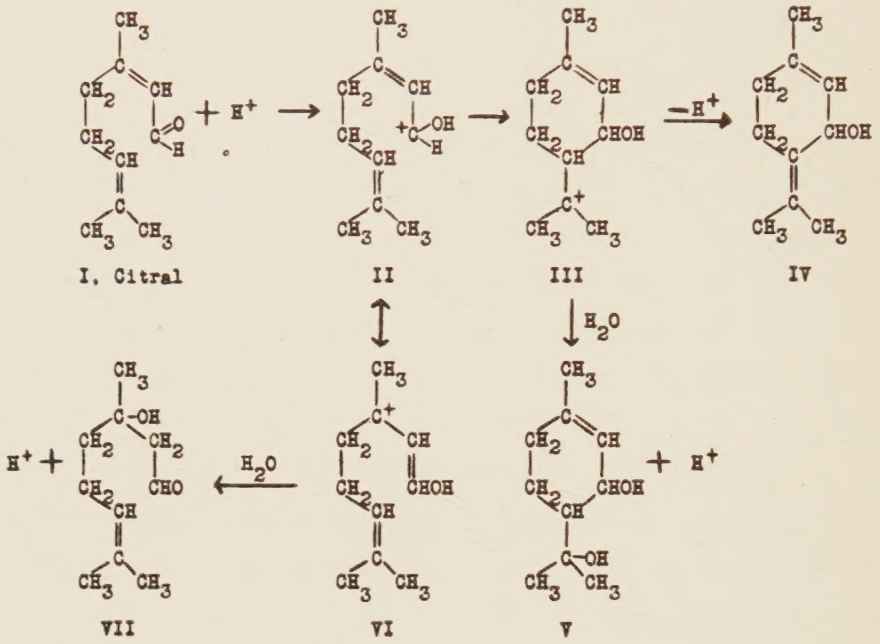
$$I_2 + 2\,S_2O_3^{=} \longrightarrow 2\,I^- + S_4O_6^{=}$$

It was found that one of the double bonds of citral disappears, and that the disappearance is first order with respect to citral concentration and first order with respect to hydrogen ion concentration. The rate of disappearance of one double bond at 25° and at 45° was in good agreement with the rate of disappearance of the aldehyde group.

The rate of disappearance of citronellal was followed by the hydroxylamine

sulfate method. It was found that citronellal disappears approximately five hundred times as rapidly as does citral.

Since the carbonyl group and one double bond of citral disappear at the same rate, it seems reasonable to assume that they disappear by mutual reaction. This is presumably a cyclization reaction, since p-cymene has been isolated from the reaction. The following mechanism is suggested.



The intermediate cation, II, could stabilize itself by acquiring a pair of electrons from the double bond to give the cation, III. This could, in turn, add water to give the glycol, V, or lose a proton to give the cyclic alcohol, IV. The cation, II, could also stabilize itself by hydration of its resonance form, VI, giving the hydroxy-aldehyde, VII.

Citronellal, which is 2,3-dihydrocitral, would be expected to cyclize more rapidly than citral, since in this case, the intermediate cation corresponding to II would have no possibility of resonance, and thus could not be stabilized by hydration.

Several other mechanisms have been suggested for the cyclization of citral.[2,3,4,5] The above mechanism is preferred because (1) it explains the role of the acid and accounts for the observed kinetics, (2) it predicts that citronellal would cyclize more rapidly than citral, and (3) it explains the change

in the course of the acid-catalyzed cyclization to yield the cyclocitrals when the aldehyde group is protected.

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VITA

The author was born in La Salle, Illinois, on January 25, 1919. After attending various public schools, she entered the University of Illinois, and was graduated in June, 1940. In September of that year she entered the Graduate School of Columbia University, where she held a Residence Fellowship and a teaching assistantship. From August, 1941, till June, 1942, she was employed as a Research Assistant at the Illinois State Geological Survey. In June, 1942, she entered the Graduate School of the University of Illinois as a Special Research Assistant. She received the degree of Master of Science in June, 1943. For the next four semesters she held a Coca Cola Company Fellowship.